FLEXIBLE MICROCHANNELS WITH INTEGRATED NANOPOROUS MEMBRANES FOR FILTRATION AND SEPARATION OF MOLECULES AND PARTICLES

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ABSTRACT

This paper reports on the technology development and characterization of polyimide-based, microfluidic channels with integrated nanoporous membranes. A layer transfer and lamination technique is used to fabricate flexible microchannels from spin-on polyimide. The microfluidic channels can be operated at high pressures and flow rates without leakage. Nanopores are created in the polyimide channel walls irradiation with swift heavy ions and subsequent chemical etching of the ion tracks. The irradiation and etching parameters can be used to adjust pore density (by ion fluence) and pore length (via ion energy). The track etching conditions, such as pH-value, concentration, temperature and etch time, define the pore diameter and pore geometry. Typical diameters of cylindrical pores range from 10 nm to 1 or 2 µm. The devices can be used for cross-flow filtration of particles and molecules in fluids or as bio-implants for drug delivery.

INTRODUCTION

Porous materials for MEMS structures have gained interest in the field of filtration and drug delivery. Nanoporous, silicon-based devices have been fabricated for immunoisolation and bio-separation by different techniques [1, 2]. In contrast, polymer-based, porous MEMS devices were mostly obtained by the integration of pre-fabricated membranes into the final device [3].
Porous polymer materials for MEMS applications can be fabricated by several methods. Pyrolysis is one way to obtain a porous membrane, where copolymers consisting of thermally stable and labile blocks are used and pore formation is effected by thermolysis of the thermally labile block [4]. Another well-known technology to generate pores in polymers is ion irradiation and subsequent ion-track etching by chemical solutions. High-energy ions leave a trace of damaged chains when passing through a polymer. By appropriate chemicals this latent track can be selectively etched and enlarged to sub-micron capillaries of very high aspect ratio. This process is routinely used by industry to generate micro-, ultra-, and nanofiltration membranes in a wide range of polymers, such as polycarbonate (PC), polyethylene terphthalate (PET) [5] and polyimides (PI, e.g. Kapton™ or Upilex™) [6]. Polyimides are routinely used in microfabrication and offer advantages over many other polymers, due to their excellent chemical and thermal stability, low water uptake, and good biocompatibility [7].

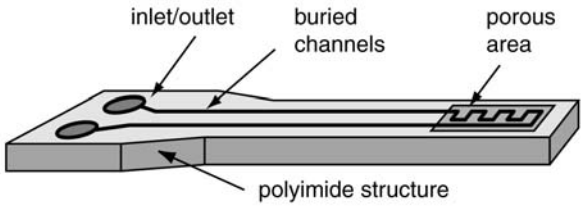

Fig. 1: Example of application: Flexible polyimide micro-needle with nanoporous filter area at the tip.

Here we propose a new approach. By combining polyimide-based microfabrication, ion irradiation and ion-track etching we have achieved monolithic integration of nanoporous membranes in flexible, microfluidic channels (Fig, 1). A layer transfer and lamination technique is applied to fabricate flexible microchannels from spin-on polyimide. The polyimide channel walls are then transformed into nanoporous membranes by ion irradiation and latent track etching. Final devices can be used for separation of molecules and particles and other biomedical applications.

MICROCHANNEL FABRICATION

A layer transfer and lamination technique is used to fabricate flexible microfluidic channels as previously described in detail [8]. In a first step, for the later release of the flexible microchannels, chrome (20 nm, adhesion layer), and sacrificial aluminum (500 nm) are evaporated on 100 mm diameter silicon substrates. On the aluminum surface, a 5 to 20 µm thick layer of photosensitive polyimide (PI-2732, DuPont) is applied, photostructured and cured. A second layer of photosensitive polyimide with a thickness between 5 and 30 µm defines the channel geometries. It is spin coated, photostructured and partially imidized at 150°C on top of the first layer (Fig. 2a). On a second wafer, a thin Mylar™ foil is made to adhere temporarily by means of surface tension by injecting water between the Mylar™ foil and the wafer. The foil is spin coated with a 5 to 20 µm thick film of photosensitive polyimide.

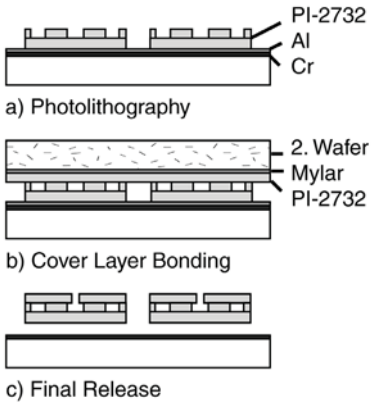

Fig. 2: Fabrication of flexible, polyimide-based microchannels by layer transfer and lamination technique.

Following a softbake step, the second substrate is flipped over and bonded to the open channel structures of the first wafer by lamination (Fig. 2b). After peeling off the Mylar™ foil, the top layer of polyimide is photostructured and the devices are cured. The resulting devices are detached from the fabrication support by anodic metal dissolution during which the sacrificial aluminum is dissolved and the chrome remains on the substrate due to the difference in the electrochemical potential (Fig. 2c).

NANOPORE FORMATION

Nanoporous membranes were monolithically integrated into the flexible microchannels by in-situ conversion of the polyimide channel walls into an ion-track etched membrane.

Ion irradiation

The polyimide microstructures were irradiated perpendicular to the channels with Xenon ions at the linear accelerator Unilac at the GSI, Darmstadt. The ion fluence ranged from 10^6 to 10^8 ions/cm^2. The energy varied between 190 and 1550 MeV depending on the thickness of Al-degrader foils placed in front of the polymer samples. The tuning of the energy was adjusted in such a way, that the ions crossed either only the top layer (Fig. 3a), or both, the top and the bottom layer of the device (Fig. 3b). Therefore, the location of the pores can be designed by the process. Ion irradiation can be completely masked with a thicker aluminum foil (e.g. 200 µm thickness) defining selected zones to be irradiated (Fig. 3c).

Pore etching process

The latent ion tracks were etched in sodium hypochlorite solutions (NaOCl, active chlorine content 13%) at different concentrations, temperatures and pH values. The pH value was adjusted by adding boric acid to the solution. As spin-on polyimide (PI-2732, DuPont) has

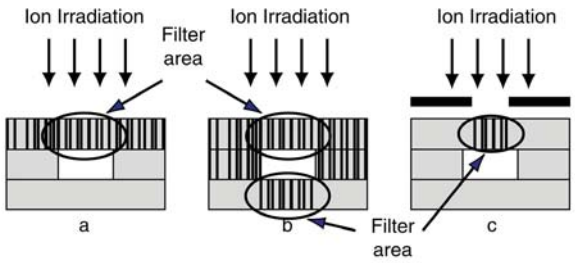

Fig. 3: Illustration of ion irradiation at low (a) and high (b) energies resulting in different penetration depths and filter areas. The effect of aluminum masking is illustrated in (c).

not previously been examined for ion-track etching, unstructured polyimide foils of 20 µm thickness were used to study the dynamics of pore formation by electrical conductivity measurement [9]. In an etching cell, the irradiated polymer foils separated two chambers filled with sodium hypochlorite as the conducting electrolyte. The conductance through the membrane is monitored as a function of etch time. The time dependence of the membrane conductance describes the pore formation and growth as the etch process develops. The breakthrough time t_b, i.e. when the etched tracks from both sides have contact, is used to calculate the etch rate along the track, v_T, by using:

$$v_T = \frac{l}{2\,t_b} \tag{1}$$

where l is the film thickness. The effective pore diameter $d_{eff}(t)$, as a function of the etching time t, can be obtained from:

$$d_{eff}(t) = \sqrt{\frac{4\,l}{\pi\,k\,N\,R_m(t)}} \tag{2}$$

where k is the specific conductivity of the etchant, N is the number of tracks in the sample and $R_m(t)$ is the measured membrane resistance. The slope off the $d_{eff}(t)$ function corresponds to the radial or bulk etch rate v_B when all pores are etched through and increase in size only radially.

RESULTS AND DISCUSSION

Polyimide microchannels were fabricated with channel widths from 30 to 500 µm, channel heights between 5 and 30 µm and lengths up to 6 cm (Fig. 4).

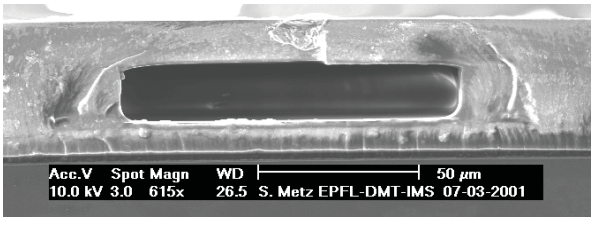

Fig. 4: Cross section of microchannel (width 100 µm, height 20 µm) showing excellent bonding between laminated layers.

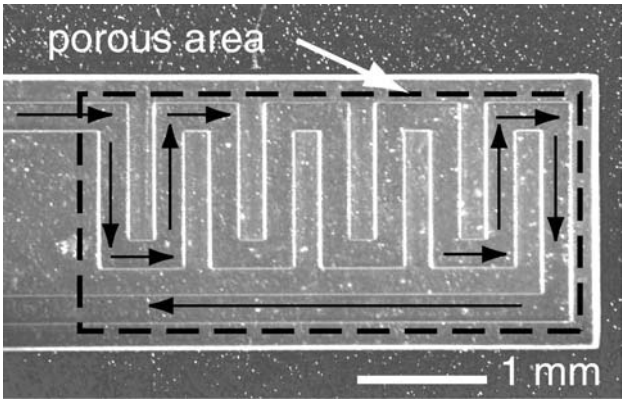

Fig. 5: Typical design with meandering channel (200 µm width) to increase filter area. The dashed line outlines the porous area and the arrows indicate fluid flow inside the microchannels.

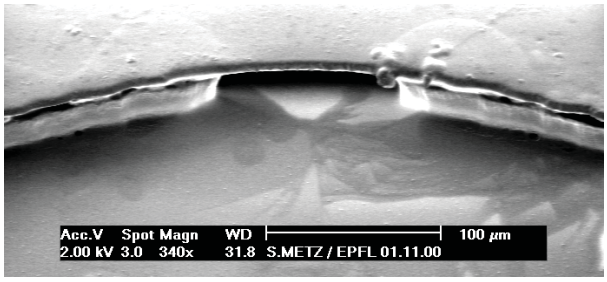

Fig. 6: Inlet into polyimide microchannel (100 µm width, 20 µm height).

The lamination technique yields a high bond strength without a visible interface between the two laminated layers (Fig. 4). The seamless adhesion is due to the incompletely imidized second layer of polyimide which enables interdiffusion with the layer to be laminated. The channels show no leakage failure and can be operated at pressures up to 19 bar [8].

Fig. 5 shows a typical design of a microchannel of 200 µm width. The meander geometry helps to increase the filter area at the tip of the microdevice (also Fig. 1).

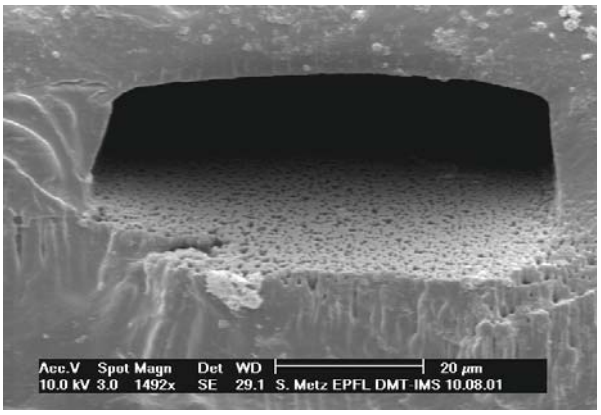

Fig. 7: Cleaved microchannel (20 µm high, 50 µm wide) with porous membrane (pore diameter 200 nm) at bottom. This corresponds to the illustration in Fig. 2a (turned upside down).

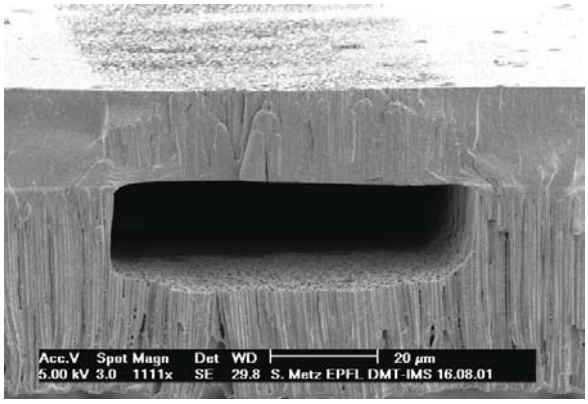

Fig. 8: Cleaved microchannel (20 µm high, 50 µm wide) with porous membrane (pore diameter 200 nm) at bottom and top. This corresponds to the illustration in Fig. 2b (turned upside down).

Fluidic interconnection is established by gluing metallic connectors on the channel inlets (Fig. 6). Fig. 7 shows a cross-section of a polyimide microchannel, where only the lower layer is perforated (corresponds to the inverted illustration in Fig. 3a). Fig. 8 shows the result of a full crossing of the ions through the device resulting in nanopores in the top and bottom polyimide layers (corresponds to the inverted illustration in Fig. 3b). By tuning the ion energy, the active filter area for cross-flow filtration applications therefore include one or two channel walls through which media is filtered.

The pore density of the membranes was controlled by varying the fluence between 10^6 to 10^8 ions/cm^2. When lower ion densities are used, the pores can be etched to larger pore radii, before neighboring tracks overlap and the membrane tends to be mechanically unstable. Here, the advantage of ion-track etched membranes lies in the possibility to adjust membrane porosity independently by two parameters: track density by irradiation fluence and pore diameter by etching parameters.

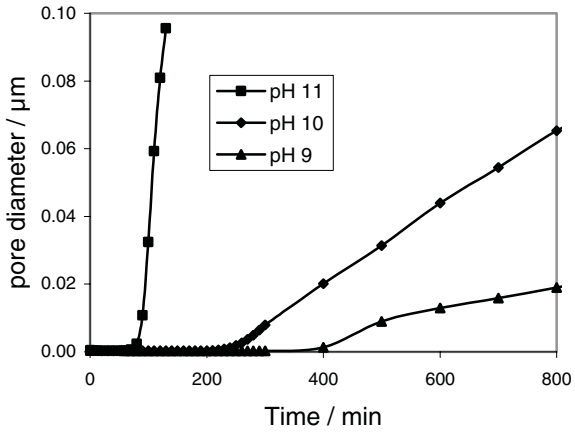

Fig. 9: Monitoring the pore opening process by electrical conductivity measurement. Breakthrough time and radial pore growth for a 20 µm polyimide foil in sodium hypochlorite solution at 54°C for different pH values.

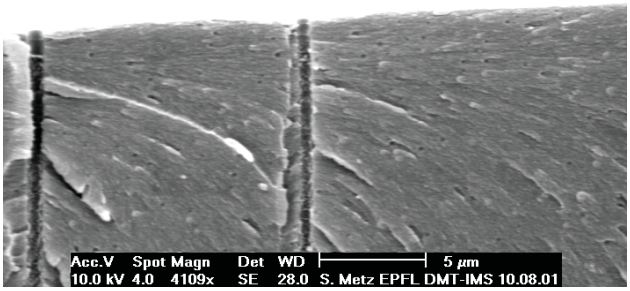

Fig. 10: Cross-section of two single pores with diameter 500 nm etched at 54°C and pH 12 for 4 hours.

During etching the pore diameter can be controlled from 10 nm to several µm by the pH value, the concentration of the etchant and the etch time. In general, the etch rates increase for higher temperatures, concentration and pH values of the etchant. A typical measurement of the effective pore diameter $d_{eff}(t)$ over time is shown for different pH values (58°C, 2 normal NaOCl solution) in Fig. 9. As long as no pores are formed, the conductance is very low. When the first pores are etched through, the conductance increases sharply indicating time of breakthrough. Then, the opening process of individual pores is masked by the statistical dispersion of pore breakthrough. When all pores are open they enlarge in diameter at constant rate as indicated by the slope. Note, the increase of the track and bulk etch rate for higher pH values (Fig. 9). The etch rate ratio v_T/v_B was found to be in the order of 1000:1 or higher indicating, a high etch selectivity.

The latent tracks in the polyimide microchannel walls were etched at pH 9.5 – 10.5 with 2 normal etch solution in order to obtain cylindrical pores with diameters ranging from 50 to 500 nm (Fig. 6, Fig. 7). The cross-section of pores are shown in Fig. 10 demonstrating that cylindrical geometry can be obtained for the given etching conditions.

CONCLUSION

We have demonstrated that polyimide-based microchannels with integrated nanoporous membranes can be fabricated by lamination and ion-track etching.

The properties of the porous membrane, such as pore density, pore depth and diameter can be controlled by the irradiation and the etching conditions. The pores in the channel top and bottom layer allow for cross-flow filtration of particles and molecules in fluids.

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